Design and Control of Network Architecture in Radiation-Curable Toughened Semi-Interpenetrating Network Resin Systems

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Design and Control of Network Architecture in Radiation-Curable Toughened Semi-Interpenetrating Network Resin Systems

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Abstract

Several issues related to the development of a radiation-curable rubber-toughened epoxy resin are investigated by performing a statistical analysis of semi-interpenetrating polymer blend formulations. The statistical analysis provided predictions for branching coefficient, copolymer molecular weight, and rubber-to-network connectivity for the B-staged interpenetrating networks. These statistical metrics relate to the properties of thermally generated B-stage networks, prior to secondary network formation using radiation cure methods such as electron beam or ultraviolet excitation. The components of these resins were described, and a procedure was developed to determine the exact weight fractions of each component that must be mixed together to achieve a desired branching coefficient and resin composition. Compositional variables include weight ratio of the two dimethacrylates, weight ratio of the two monoepoxides, and weight ratio of epoxides to dimethacrylates. Using the raw materials selected for this study, we determined that many network structures are not attainable. Specifically, it is not possible to prepare B-stage resins without the use of mono- or difunctional units, such as phenyl glycidyl ether (PGE) or methacrylated digicydyl ether of bisphenol A (bisGMA). The possible formulations are determined, and a map is proposed showing the combinations of PGE and bisGMA content that are allowed for B-stage formation.

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1. Introduction

The desire to move polymer composite manufacturing from traditional autoclave processing towards non-autoclave techniques has spawned interest in several non-thermal curing methods for thermosetting polymer systems. Recently, several curing methods have received wide attention and have shown promise as alternatives to thermal curing systems used presently. Specifically, rapid cure of cationic or free radical structural resins by electron-beam (e-beam) radiation has been identified as a breakthrough technology that may significantly reduce the costs associated with advanced composite materials. In theory, the cost reductions are derived from decreased capital investments on autoclave equipment and increased yields from reduced cure cycles. However, these arguments necessarily assume that the performance of the composites cured using e-beam irradiation will be equivalent to or better than their thermally cured counterparts. To date, the resin dominated composite properties and the properties of e-beamed adhesive joints do not meet the specified target values of the thermally cured baseline materials.

The poor performance of the e-beamed materials has been attributed to a number of effects. Poor resin properties and questionable resin-reinforcement adhesion have been identified as probable causes for substandard mechanical properties. Most notably, the resins that have been developed to date have been very brittle. Consequently, major efforts have been directed at improving the toughness of cationic epoxy-based electron beam resins. The goals of these programs have been to meet the performance standards obtained using thermally cured aerospace-grade-toughened epoxy prepreg materials. While some progress has been made through these efforts, it is clear that a good balance between toughness, modulus, and service temperature has not been achieved.

To date, this research has focused on the use of cationic resins. Various approaches have been used to toughen cationic resins with moderate success. Unfortunately, many of the methods that are available to toughen thermally cured epoxies are not possible with cationic e-beam systems. The types of two-phase morphologies associated with toughened epoxies are difficult to achieve with these e-beam systems. Furthermore, the possibility and methods of chain extension of cationic epoxies are not well understood. Therefore, the synergistic effects of second phase toughening and chain extension in the host matrix cannot be capitalized in the e-beam systems. Flexibilizers have been used effectively to toughen these systems. Not surprisingly, this approach results in unacceptable decreases in glass transition temperatures and ultimate service temperatures. Efforts to toughen these resins continue and hopefully suitable resins will be developed.

The specific work described previously has summarily dismissed the use of free radical curing systems for composite applications due to bad experiences with excessive shrinkage, poor modulus retention, and brittleness. Yet, concurrent with the cationic toughening research, new innovative approaches have solved many of the problems previously associated with free radical curing e-beam resins. The use of sequential interpenetrating networks (S-IPNs) has substantially improved the properties of free radical systems. Previous researchers have used the S-IPN method to produce resins with low shrinkage, high toughness, and good translation to composite properties [1, 2]. This approach is not a wholly e-beam curing method, but rather a thermal-radiation dual cure hybrid solution that may prove useful in many applications.

The S-IPN approach has been reported elsewhere and will only be reviewed here. Figure 1 shows the S-IPN cure mechanisms schematically. Essentially, the resin consists of several components that are selected to provide a balance of processing ease with good end-use properties. After initial mixing of the components, the resins are first cured at slightly elevated temperatures (around 60 °C). During this stage, the thermally curing monomers will react to form a highly branched (or gelled) copolymer that is swelled by the unreacted dimethacrylates. Typical chemistries used in the condensation step include epoxy-amine and isocyanate-polyol (polyurethane) systems. The condensation reaction proceeds to completion and remains relatively stable until further reacted by exposure to radiation.
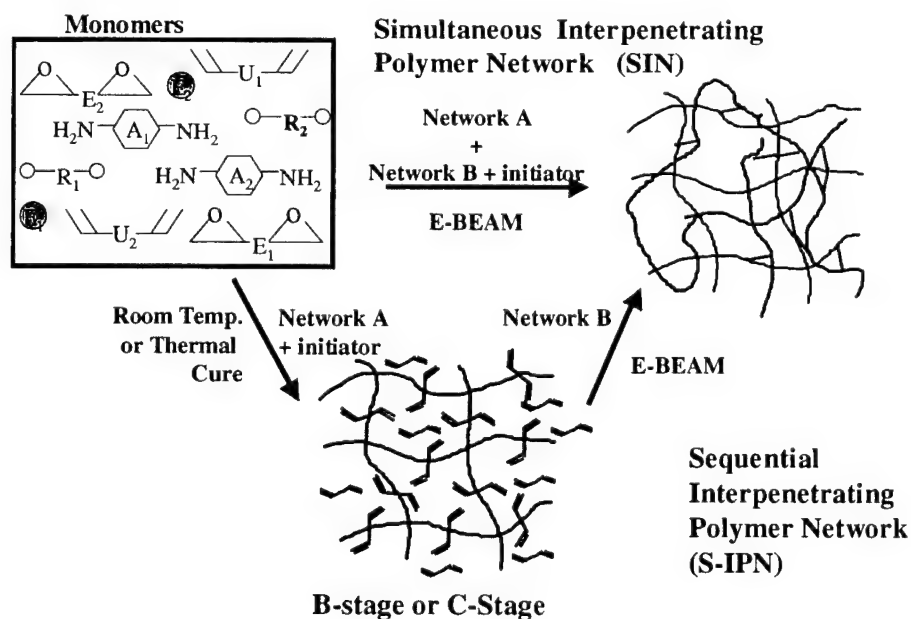

Figure 1. Methods of achieving interpenetrating polymer networks in one- and two-step cure cycles.

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If the thermal curing reaction completes prior to the critical conversion for gelation, the material is commonly referred to as a "B-staged" resin. At this point, the resin will be a highly viscous liquid. Physically, this material is a mixture of a highly branched polydisperse polymer and unreacted free radical monomers. It can be produced by either controlling the degree of branching by appropriate selection of starting monomers or by freezing the reaction prior to gelation. Beyond the gel point, the material is referred to as the "c-stage," which is a gelled network that is swollen by the unreacted free radical monomers. The nature of this network will greatly control the structure and properties of the final e-beamed material and permits great flexibility to influence processibility and final performance.

After the thermal reaction has completed, the resin is irradiated by an electron beam source. (Alternatively, ultraviolet radiation could be used for this purpose.) This radiation "post-bake" fully cures the free radical portion of the S-IPN to form the final structure. The properties of the fully cured S-IPN are determined by controlling the structure of the monomer building blocks. Materials ranging from compliant elastomeric networks to high glass transition temperature ($T_g \sim 180$ °C) resins can be produced. Also, importantly, the ability to control the molecular weight distribution during the condensation stage of the polymerization permits the use of traditional secondary phase toughening, which results in superior composite and adhesive properties.

The purpose of this report is to document the materials' design strategies that permit careful control of the network structure. Due to the complicated nature of these resins, a linear system of equations has been derived to describe the composition and stoichiometry of the S-IPN resins. Furthermore, this approach will be used to determine optimum compositions for phase separation of elastomeric or thermoplastic tougheners. This materials-by-design approach was absolutely necessary to achieve the chemistry and microstructure that provided the required performance levels for adhesive and composite applications.

In this work we will focus on S-IPNs comprised of a thermally cured epoxy-amine network and a combination of two different free radical monomers. In some cases, a reactive elastomer will be incorporated into the system to provide enhanced toughness. In general, the S-IPN resins will have five or more components including mono- and diepoxide monomers, diamine curing agents, reactive polymeric rubber, and dimethacrylate monomers. If reactive rubber tougheners are used, it is desired that the rubber phase separates from the other components during the initial epoxy-amine cure. These rubber particles are known to significantly improve the fracture toughness of epoxy resins without severely reducing the service temperature of the base resin [3]. Upon electron beam irradiation, an interconnected, interpenetrating network of epoxy and dimethacrylate units is created. After the resins are fully cured, they are hard solids, and no further change in the morphology of the rubber particles is

possible. This is an essential feature of second phase-toughened thermosets. Rubber that remains dissolved in the host matrix will not effectively toughen the resin and will also have a deleterious effect on T_g.

The objectives of this work are to (1) develop a procedure for determining the proper amounts of each component to be added to the resin, (2) predict the conditions which will result in phase separation of the rubber, and (3) investigate the coalescence of rubber particles in the B-stage resin over time.

A procedure was developed to determine appropriate resin formulations as a function of several input parameters such as desired rubber weight fraction and dimethacrylate composition. The time-dependent coalescence of rubber particles will depend on the mobility of the rubber molecules. Their mobility will be severely affected by the degree to which they are connected to the copolymer and the average molecular weight of the copolymer. Predictions of connectivity and molecular weight are derived by use of a statistical analysis of the copolymer during cure but prior to gelation. A thermodynamic analysis was carried out to investigate the conditions that will lead to phase separation of the B-stage resin. Also briefly presented are results of the effect of electron beam exposure on the properties of the rubber and results of an oxidation study of nickel particles.

2. Design of Network Structure

The desired attributes of the resin will determine the appropriate formulation (i.e., the weight fractions of the components). A major advantage of these S-IPN structures is the ability to tailor the properties of the network structure to achieve desirable properties in the final product. These include rubber fraction, epoxy/amine stoichiometric balance, branching coefficient the resin after thermal cure, branching coefficient after complete cure, the fraction of epoxy-amine versus free radical species, and relative fractions of the different dimethacrylates. The use of at least two dimethacrylates (one aromatic and one aliphatic) allows for better control of the viscosity of the resin. An added advantage of the S-IPN approach is that the two networks can be linked to one another by using a multifunctional monomer that acts as a coupling agent between the thermal curing and radiation curing networks. It is believed that this coupling is partially responsible for the reduction in cure shrinkage and improved mechanical properties of the S-IPN compared to traditional free radical systems.

The S-IPN systems that are described here are very complicated and comprised of many different components. Traditional formulation of thermoset resins is usually limited to a few components and optimized empirically or using very simplistic design rules. For example, in amine cured epoxies, the stoichiometry is usually balanced between the epoxies and amines that are used in a given

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formulation. In the materials described here, this simple constraint must be balanced to accommodate coupling monomers, non-reactive diluents, rubber modifiers, and controlled branching coefficients. The control and balance of these features will ultimately control the toughness, modulus, and service temperature of these resins. Therefore a more elegant network design approach must be used to assist in the formulation of these resins.

The design of the network structure is a formulation procedure based on the fact that n conditions must be specified in order to determine the weight fractions of n components. These conditions will ensure that the desired attributes are attained. The resins of interest and the procedure for determining their formulations will now be explained. This procedure specifically applies to a resin containing the types of components listed in the next section for both B-staged one-part resins and gelled (C-staged) resin types. It is hoped that this methodology will be presented in such a way that it could easily be modified to apply to similar resins containing any components of interest. Limitations and assumptions of this model will be presented next.

2.1 Materials

2.1.1 Diepoxides

The primary diepoxide that has been employed is a diglycidyl ether of bisphenol A (DGEBA) supplied by Shell as Epon 828. This will be referred to as 828. $M = 390$ g/mol. Additionally, higher molecular weight DGEBA resins are used in instances to impart greater flexibility and to chain extend the epoxy network when necessary. These will be identified as they are used.

2.1.2 Amine Curing Agent

The curing agent is bis(p-aminocyclohexyl)methane supplied by Air Products as PACM-20. This will be referred to as PACM. $M = 210$ g/mol.

2.1.3 Monoepoxides

These monomers have only one functional group and are used to control branch structure in the B-stage resin. Specifically, phenyl glycidyl ether (PGE), supplied by Shell as HELOXY 63 Modifier, was used to prevent gelation of the one-part extended shelf-life resin formulations. $M = 150$ g/mol.

2.1.4 Liquid Elastomers

Several different rubbers were used in this study. Primarily end-functionalized butyl nitrile rubbers were used. These materials are random copolymers of butadiene and acrylonitrile containing typically 18% acrylonitrile by mole with reactive chain terminators. The types of end-group functionality that were examined here included epoxy and amine groups. The epoxy-terminated

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materials (ETBN) were generally provided as a mixture of the rubber and DGEBA and were obtained from Shell Chemicals. Amine-terminated butyl nitrile (ATBN) rubber was supplied by B. F. Goodrich as Hycar 1300. It has a number average molecular weight of 3900 and is difunctional.

2.1.5 Dimethacrylates

Two dimethacrylates are used. One is fully methacrylated diglycidyl ether of bisphenol A supplied by Sartomer (CN 151) and referred to as bisGMA. The other is 1,6 hexanediol dimethacrylate supplied by Sartomer (SR 239) and referred to as HDDMA. Differing amounts of these can be used to control the viscosity of the B-stage resin. $M_{HDDMA} = 254$ g/mol; $M_{bisGMA} = 552$ g/mol.

2.1.6 Dual Functional Monomer (DFM)

This is a DGEBA molecule in which one epoxide group has reacted with methacrylic acid and therefore is a monoepoxide. The unreacted epoxide group on the DFM is free to react with an amine during the formation of the S-IPN, while the methacrylated end is capable of reacting with other methacrylates during irradiation. During synthesis, if the mole ratio of methacrylic acid to DGEBA, R, is less than two, there will be three different products of this reaction. Some DGEBA will partially react producing one the DFM unreacted epoxide group and one methacrylate group. A statistical-portion DGEBA will not participate in the reaction and keep two unreacted epoxy groups. Consequently, some DGEBA will become fully methacrylated. (If Epon 828 is used as the DGEBA, this product is identical to the bisGMA dimethacrylate supplied by Sartomer.) The mixture of these products is designated ARL1015. The mole fractions of Epon 828, DFM, and bisGMA in the ARL1015 are given, respectively, by $(1-R/2)^2$, $R(1-R/2)$, and $(R/2)^2$. If Epon 828 is used, the $M_{DFM} = 466$ g/mol.

2.2   Resin Specifications for Producing B-Staged IPN Resins

In order to determine the appropriate mixing proportions of the starting materials, the following parameters must be specified:

2.2.1 Composition of ARL1015

As stated above, the molar fractions are determined by R, the initial mole ratio of methacrylic acid to diepoxide used in the production of ARL1015 [4, 5]. The weight fractions for the diepoxide, dimethacrylate, and difunctional monomer (x_{DE}, x_{DE}, x_{DE}), respectively, are calculated as follows.

$$x_{DE} = (1 - R/2)^2 \frac{MW_{DE}}{MW_{DFM}}$$

$$x_{DM} = (R/2)^2 \frac{MW_{DM}}{MW_{DFM}}$$

$$x_{DFM} = R(1 - R/2) \frac{MW_{DFM}}{MW_{DFM}} = R(1 - R/2).$$

2.2.2 Branching Coefficient of B-Stage Resin, α_B

In order to prevent the B-stage resin from gelling, α_B must be lower than $1/(1-f)$, where f is the functionality of the curing agent. PACM is tetrafunctional, so α_B must be specified to be below 1/3. This can be done in two ways. First, it can be done by stopping the reaction prior to the critical conversion for gelation. Alternatively, active hydrogens on the amine curing agent can be end-capped with monofunctional epoxies so that only 1/3 of the active groups react with an difunctional epoxy. Upon conversion completion, all amine hydrogens will have reacted without gelation, creating a viscous highly branched copolymer mixed with the methacrylates. In this work we will use the second method since it will produce a more highly stable B-staged product.

2.2.3 Rubber Fraction, w_{rubber}

This is the desired overall weight fraction of rubber in the resin.

2.2.4 Matrix Composition, β

This is defined as the epoxide network weight (excluding DFM) divided by total weight (excluding DFM and rubber).

$$\beta = \frac{w_{PACM} + w_{828} + x_{DE}w_{1015} + w_{PGE}}{w_{PACM} + w_{828} + w_{PGE} + w_{bisGMA} + w_{HDDMA} + (1 - x_{DFM})w_{1015}}.$$

2.2.5 Monoepoxide Composition, γ

This is defined as the weight of PGE divided by weight of both monoepoxides (PGE and DFM).

$$\gamma = \frac{w_{PGE}}{w_{PGE} + x_{DFM}w_{1015}}.$$

2.2.6 Dimethacrylate Composition, δ

This is defined as the weight of bisGMA divided by weight of both dimethacrylates (bisGMA and HDDMA).

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$$\delta = \frac{w_{bisGMA} + x_{DM} w_{1015}}{w_{bisGMA} + x_{DM} w_{1015} + w_{HDDMA}} \, .$$

2.3 Resin Formulation

For the one-part B-staged resins studied here, seven ingredients will comprise the mixture. These seven required weight fractions $(w_{828}, w_{PACM}, w_{ATBN}, w_{1015}, w_{PGE}, w_{bisGMA}, w_{HDDMA})$ are determined by the simultaneous solution of seven equations which are based on stoichiometric and mass balances and the previous specifications.

The actual weight fractions of Epon 828 and bisGMA present in the resin will be larger than the computed values of w_{828} and w_{bisGMA} because these species are also present in ARL1015.

2.3.1 Stoichiometric Balance

For these resins, an exact stoichiometric balance of amines and epoxides is desired. Each PACM is capable of reacting with four epoxides and each ATBN with two. Therefore the following equation must be satisfied:

$$\frac{w_{PACM}}{EW_{PACM}} + \frac{w_{ATBN}}{EW_{ATBN}} - \frac{w_{828}}{EW_{828}} - \frac{x_{DE} w_{1015}}{EW_{DE}} - \frac{x_{DFM} w_{1015}}{EW_{DFM}} - \frac{w_{PGE}}{EW_{PGE}} = 0 \, , \qquad (1)$$

where EW_i is the equivalent weight of i and is equal to the molecular weight of i divided by the functionality of i.

2.3.2 Branching Coefficient

The branching coefficient α_B of the epoxy copolymer in the B-stage resin is a nonlinear function of the weight fractions. From section 3.1, it is known that $\alpha_B = p_{828} p_{PACM} / (1 - p_{828} p_{ATBN})$. This equation is nonlinear in the weight fractions and can be written as

$$\alpha_B \left[\left(\frac{w_{PACM}}{EW_{PACM}} + \frac{w_{ATBN}}{EW_{ATBN}} \right)^2 - \frac{\left(w_{828} + x_{DE} w_{1015} \right) w_{ATBN}}{EW_{828} EW_{ATBN}} \right]$$
$$- \frac{\left(w_{828} + x_{DE} w_{1015} \right) w_{PACM}}{EW_{828} EW_{PACM}} = 0 \, . \qquad (1a)$$

If p_{ATBN} is small (it is typically around 0.05 for these resins), then p_{PACM} is close to 1 and α_B is approximately equal to $\alpha_B' = p_{828}$. This leads to the following linear equation:

$$\frac{w_{PACM}}{EW_{PACM}} + \frac{w_{ATBN}}{EW_{ATBN}} - \frac{1}{\alpha_B'} \frac{\left(w_{828} + x_{DE} w_{1015} \right)}{EW_{828}} = 0 \, . \qquad (2)$$

2.3.4 Rubber Fraction

Specification of the overall rubber weight fraction requires that

$$w_{ATBN} = w_{rubber}.$$ (3)

2.3.5 Matrix Composition

This specification is rewritten as

$$(1-\beta)w_{PACM} + (1-\beta)\left(w_{828} + x_{DE}w_{1015}\right) + (1-\beta)w_{PGE}$$
$$-\beta\left(w_{bisGMA} + x_{DM}w_{1015}\right) - \beta w_{HDDMA} = 0.$$ (4)

2.3.6 Monoepoxide Composition

This specification is rewritten as

$$(1-\gamma)w_{PGE} - \gamma\, x_{DFM}w_{1015} = 0.$$ (5)

2.3.7 Dimethacrylate Composition

This specification is rewritten as

$$(1-\delta)\left(w_{bisGMA} + x_{DM}w_{1015}\right) - \delta\, w_{HDDMA} = 0.$$ (6)

2.3.8 Mass Balance

All the weight fraction must sum to one.

$$w_{PACM} + w_{ATBN} + w_{828} + w_{1015} + w_{PGE} + w_{bisGMA} + w_{HDDMA} = 1.$$ (7)

Equations 1–7 can be written in matrix form.

$$\mathbf{A}\begin{Bmatrix} w_{828} \\ w_{PACM} \\ w_{ATBN} \\ w_{1015} \\ w_{PGE} \\ w_{bisGMA} \\ w_{HDDMA} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ w_{rubber} \\ 0 \\ 0 \\ 0 \\ 1 \end{Bmatrix},$$ (8)

where

$$A = \begin{bmatrix} \dfrac{-1}{EW_{828}} & \dfrac{1}{EW_{PACM}} & \dfrac{1}{EW_{ATBN}} & -\dfrac{x_{DE}}{EW_{DE}} - \dfrac{x_{DFM}}{EW_{DFM}} & \dfrac{-1}{EW_{PGE}} & 0 & 0 \\[2ex] \dfrac{-1}{\alpha' EW_{828}} & \dfrac{1}{EW_{PACM}} & \dfrac{1}{EW_{ATBN}} & \dfrac{-x_{DE}}{\alpha' EW_{DE}} & 0 & 0 & 0 \\[2ex] 0 & 0 & 1 & 0 & 0 & 0 & 0 \\[1ex] 1-\beta & 1-\beta & 0 & (1-\beta)x_{DE} - \beta x_{DM} & 1-\beta & -\beta & -\beta \\[1ex] 0 & 0 & 0 & -\gamma x_{DFM} & 1-\gamma & 0 & 0 \\[1ex] 0 & 0 & 0 & (1-\delta)x_{DM} & 0 & 1-\delta & -\delta \\[1ex] 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \tag{8a}$$

The weight fractions of the starting materials that satisfy the specifications listed previously are found by solving equation 8.

Using this procedure, it is not possible to specify α_B exactly because of the use of equation 2. After computation of the weight fractions, the real value of α_B should be computed (see section 3.1) to ensure that it is less than 1/3 and close to the desired value. If this value is unacceptable, a new value of α_B' should be specified and α_B checked again.

2.4 Discussion

Because both Epon 828 and bisGMA are always present in ARL1015, some formulations are not possible. As stated previously, the mole fractions of Epon 828, DFM, and bisGMA in the ARL1015 are given, respectively, by $(1-R/2)^2$, $R(1-R/2)$, and $(R/2)^2$, where R is the molar ratio at which methacrylic acid and Epon 828 are mixed in the production of ARL1015. The presence of the difunctional Epon 828 in ARL1015 is undesirable because the ratio of diepoxides to monoepoxides must be kept low to avoid gelation of the B-stage resin. If the molar ratio of Epon 828 to DFM in ARL1015 is too large, PGE must be added to the resin to prevent gelation. This is undesirable because PGE will not react with the methacrylate network during final curing and the properties of the resin will suffer. If R = 1, the molar ratio of Epon 828 to DFM in ARL1015 is 1/2.

For larger values of R, this ratio decreases, but the fraction of bisGMA increases. The possible formulations which can be made with $\alpha_B = 0.3$ and $\beta = 0.5$ are shown in Figure 2. This figure shows combinations of the weight fraction of PGE in the resin and δ which are possible when using ARL1015 made with different values of R. Recall that δ is the fraction of the dimethacrylates that are bisGMA.
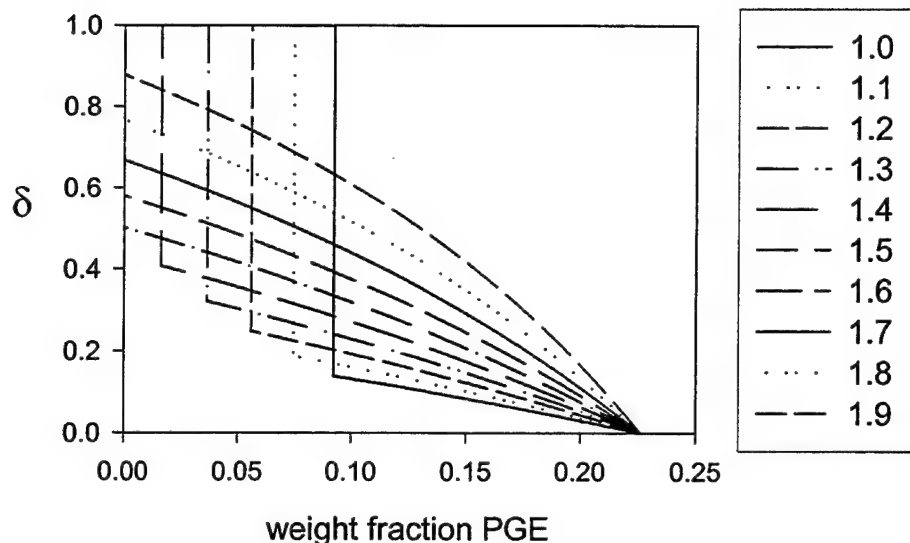
Figure 2. Map of possible formulations for $\alpha_B = 0.3$ and $\beta = 0.5$ for different values of R (legend).

For low values of R (<1.5), some amount of PGE must always be added to the resin to ensure that $\alpha_B = 0.3$. For larger values of R (e.g., R ≥ 1.5), PGE does not need to be added, but the minimum value of δ will be greater than 0.5. This will limit the extent to which the viscosity of the B-stage resin can be controlled. Therefore, a compromise between minimum PGE and bisGMA contents in these resins must be made.

3. Statistical Analysis of Network Development

The mobility or diffusivity of the rubber in the B-stage resin will determine the extent to which rubber particles can form *via* phase separation and the rate at which these particles can coalesce with time. The diffusivity of the rubber is very dependent on the size and structure of the molecules of which it is a part. The extent to which the rubber is connected to the epoxy copolymer will also affect the extent to which epoxy units are incorporated into the rubber particles and the adhesion between the rubber particles and the matrix.

Consider the copolymer obtained by complete reaction of PACM, Epon 828, DFM, PGE, and ATBN. Recall that PACM is a tetrafunctional amine, ATBN is a difunctional amine, Epon 828 is a difunctional epoxide, and PGE and DFM are monofunctional epoxides.

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Define p_{828}, p_{DFM}, and p_{PGE} as the fraction of epoxides which belong to Epon 828, PGE, and DFM, respectively. These are

$$p_{828} = \frac{\dfrac{2w_{828}}{M_{828}}}{\dfrac{2w_{828}}{M_{828}} + \dfrac{w_{DFM}}{M_{DFM}} + \dfrac{w_{PGE}}{M_{PGE}}} \qquad p_{DFM} = \frac{\dfrac{w_{DFM}}{M_{DFM}}}{\dfrac{2w_{828}}{M_{828}} + \dfrac{w_{DFM}}{M_{DFM}} + \dfrac{w_{PGE}}{M_{PGE}}}$$

$$p_{PGE} = \frac{\dfrac{w_{PGE}}{M_{PGE}}}{\dfrac{2w_{828}}{M_{828}} + \dfrac{w_{DFM}}{M_{DFM}} + \dfrac{w_{PGE}}{M_{PGE}}},$$

where w_i and M_i are the weight fraction and molecular weight of component i. After all epoxides and amines have reacted, these fractions will equal the probability that an amine hydrogen chosen at random has reacted with these species.

Similarly, define p_{PACM} and p_{ATBN} as the fraction of amine hydrogen atoms, which belong to PACM and ATBN, respectively. These are

$$p_{PACM} = \frac{\dfrac{4w_{PACM}}{M_{PACM}}}{\dfrac{4w_{PACM}}{M_{PACM}} + \dfrac{2w_{ATBN}}{M_{ATBN}}} \quad \text{and} \quad p_{ATBN} = \frac{\dfrac{2w_{ATBN}}{M_{ATBN}}}{\dfrac{4w_{PACM}}{M_{PACM}} + \dfrac{2w_{ATBN}}{M_{ATBN}}}.$$

3.1 Branching Coefficient

The branching coefficient α_B of the copolymer is defined as the probability that any functional unit on a multifunctional monomer $(f > 2)$ is connected *via* a chain of difunctional units to another multifunctional monomer [6]. The only multifunctional monomer is this case is PACM $(f = 4)$.

Each amine functional unit can be connected to one of the following three structural units.

(1) A pendant chain containing i 828 units, i ATBN units, and 1 PGE unit

$$-[828 - ATBN]_i - PGE.$$

(2) A pendant chain containing i 828 units, i ATBN units, and 1 DFM unit

$$-[828 - ATBN]_i - DFM.$$

(3) A linkage chain containing $i+1$ 828 units and i ATBN units that are connected to a PACM unit

$$-[828 - ATBN]_i - 828 - PACM.$$
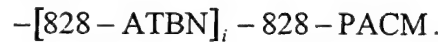
The probability p_1 that an amine functional unit is connected to (1) is

$$p_1(i) = \left(p_{826} p_{ATBN}\right)^i p_{PGE}.$$

Similarly,

$$p_2(i) = \left(p_{828} p_{ATBN}\right)^i p_{DFM}$$

$$p_3(i) = \left(p_{828} p_{ATBN}\right)^i p_{828} p_{PACM}.$$

The probability that an amine functional unit is connected to 1 with any value of i equals

$$P_1 = \sum_{i=0}^{\infty} \left(p_8 p_a\right)^i p_g = \frac{p_g}{1 - p_8 p_a}.$$

Similarly,

$$P_2 = \sum_{i=0}^{\infty} \left(p_8 p_a\right)^i p_m = \frac{p_m}{1 - p_8 p_a}$$

$$P_3 = \sum_{i=0}^{\infty} \left(p_8 p_a\right)^i p_8 p_p = \frac{p_8 p_p}{1 - p_8 p_a}.$$

As a check, it can easily be shown that $P_1 + P_2 + P_3 = 1$. Since P_3 is the probability that an amine functional group is connected to a multifunctional PACM unit, it is also equal to the branching coefficient, α_B.

3.2 Molecules Containing PACM Units

Any molecule containing a PACM unit must be considered a branched copolymer molecule. The properties of the copolymer will depend on the fraction of pendant and linkage chains that contain the flexible ATBN units. The fraction of these pendant and linkage chains that contain at least n ATBN units is given by

$$\frac{\sum\limits_{i=n}^{\infty} P_1 + \sum\limits_{i=n}^{\infty} P_2 + \sum\limits_{i=n}^{\infty} P_3}{\sum\limits_{i=0}^{\infty} P_1 + \sum\limits_{i=0}^{\infty} P_2 + \sum\limits_{i=0}^{\infty} P_3} = \left(p_8 p_a\right)^n,$$

where

$$\sum_{i=n}^{\infty} p^i = \frac{p^n}{1 - p}.$$

For a typical resin formulation, $p_{828} = 0.3$ and $p_{ATBN} = 0.05$. Therefore, the fraction of pendant and linkage chains that contain at least one ATBN unit is 0.015, and the fraction of chains that contain at least two ATBN units is 2.25×10^{-4}.

3.3 Molecules Containing ATBN Units

There are two types of molecules that may contain ATBN units: branched and linear. The linear molecules must not contain any PACM units. Since ATBN also has an amine functionality, the probability that an ATBN functional group is connected *via* a linkage chain to a PACM unit is equal to α_B. The probability that *both* ends of an ATBN unit are *not* connected to a PACM (*i.e.*, it is part of a linear molecule) is equal to $(1 - \alpha_B)^2$, and the probability that an ATBN unit is connected to a PACM (*i.e.*, it is part of a branched molecule) is $1 - (1 - \alpha_B)^2$.

For a typical value of α (0.3), 51% of the ATBN units are connected to a PACM (*i.e.*, a branched copolymer) and 49% of the ATBN units are part of a linear chain.

3.4 Linear Structural Units

After full epoxy reaction, there will be three types of linear structures:

- links between two PACM units,
- pendant chains connected to one PACM unit, and
- linear chains not connected to PACM (must contain at least one ATBN unit).

Because each of these must contain an epoxy, the distribution of these three types of chains can be determined as follows: pick an epoxy group at random and determine the probability that it belongs one of the three types listed previously.

If a diepoxide (828) is found, all three types are possible. They are

(1) A linkage chain containing an 828 reacted with i ATBN, i 828, and one PACM on one side and j ATBN, j 828, and 1 PACM on the other side;

$$PACM - [828 - ATBN]_i - 828 - [ATBN - 828]_j - PACM.$$
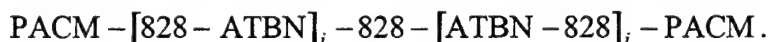
(2) A pendant chain containing an 828 reacted with i ATBN, i 828, and one PACM on one side and $j+1$ ATBN, j 828 units, and one end cap unit (PGE or DFM) on the other side;

$$PACM - [828 - ATBN]_i - 828 - [ATBN - 828]_j - ATBN - CAP.$$
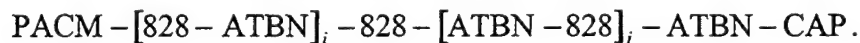
(3) A linear chain containing an 828 reacted with $i+1$ ATBN, i 828, and one end cap unit on one side and $j+1$ ATBN, j 828, and one end cap unit on the other side;
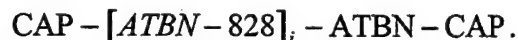
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$$CAP - ATBN - [828 - ATBN]_i - 828 - [ATBN - 828]_j - ATBN - CAP.$$
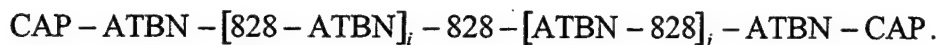
If an end cap is found, only two types are possible. They are

(4) A pendant chain containing an end cap reacted with i ATBN, i 828, and one PACM;

$$CAP - [ATBN - 828]_i - PACM.$$
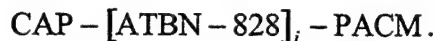
(5) A linear chain containing an end cap reacted with $i+1$ ATBN, i 828, and another end cap;

$$CAP - [ATBN - 828]_i - ATBN - CAP.$$

The probability of finding an 828 when selecting an epoxy unit at random is

$$y_{828} = \frac{n_{828}}{n_{828} + n_{CAP}},$$

where n_{828} is the number of difunctional 828 molecules and n_{CAP} is the number of end caps (*i.e.*, monofunctional epoxides). In terms of p_{828} and $y_{828} = \frac{p_{828}}{2 - p_{828}}$, the probability of finding a monofunctional epoxide when selecting an epoxy unit at random is $y_{CAP} = 1 - y_{828}$.

The probability of finding an 828 unit as part of structure (4) (connected to i ATBN/828 units and a PACM on one side and j ATBN/828 units and a PACM on the other side) is $y_{828}(p_{ATBN}p_{828})^i (1 - p_{ATBN})(p_{ATBN}p_{828})^j(1 - p_{ATBN})$ or

$$p_4(i,j) = y_{828}(1 - p_{ATBN})^2 (p_{ATBN}p_{828})^{i+j}.$$

Similarly, the probabilities of finding structures 5–8 when selecting an epoxy unit at random are

$$p_5(i,j) = 2y_{828}(1 - p_{ATBN})(1 - p_{828})p_{ATBN}(p_{ATBN}p_{828})^{i+j}$$

$$p_6(i,j) = y_{828}(1 - p_{828})^2 p_{ATBN}^2 (p_{ATBN}p_{828})^{i+j}$$

$$p_7(i) = y_{CAP}(1 - p_{ATBN})(p_{ATBN}p_{828})^i$$

$$p_8(i) = y_{CAP}p_{ATBN}(1 - p_{828}) (p_{ATBN}p_{828})^i.$$

The factor of 2 in the p_2 expression is needed because the (2) structure can have the end cap on either end and both possibilities must be considered. The probability of finding an 828 unit as part of structure (4) with any value of i or j is

$$P_4 = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} p_4(i,j) = y_{828}(1-p_{ATBN})^2 \sum_{i=0}^{\infty}(p_{ATBN}p_{828})^i \sum_{j=0}^{\infty}(p_{ATBN}p_{828})^j$$

$$= \frac{y_{828}(1-p_{ATBN})^2}{(1-p_{ATBN}p_{828})^2}.$$

Similarly, the probabilities of finding structures 5–8 with value of i or j when selecting an epoxy unit at random are

$$P_2 = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} p_2(i,j) = \frac{2y_8(1-p_a)(1-p_8)p_a}{(1-p_a p_8)^2}$$

$$P_3 = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} p_3(i,j) = \frac{y_8(1-p_8)^2 p_a^2}{(1-p_a p_8)^2}$$

$$P_4 = \sum_{i=0}^{\infty} p_4(i) = \frac{(1-y_8)(1-p_a)}{1-p_a p_8}$$

$$P_5 = \sum_{i=0}^{\infty} p_5(i) = \frac{(1-y_8)(1-p_a)p_a}{1-p_a p_8}.$$

It can be shown that these sum to one. Typical numbers for these fractions (assuming $p_{828} = 0.3$ and $p_{ATBN} = 0.05$) are

$$P_4 = 0.164, \quad P_5 = 0.012, \quad P_6 = 2.22E-4,$$

$$P_7 = 0.794, \text{ and } P_8 = 0.029.$$

The fraction of linear structures that are links between PACM is given by $P_{link} = P_4$. The fraction of linear structures that are PACM pendants are $P_{pendant} = P_5 + P_7$. The fraction of linear structures that are not connected to PACM (linear molecules) are $P_{linear} = P_6 + P_8$. Typical values for these are

$$P_{link} = 0.164, \quad P_{pendant} = 0.806, \text{ and } P_{linear} = 0.029.$$

It is also possible to calculate the average values of $i+j$ and i for each of the three structural types. For the linkages, the average number of ATBN/828 pairs is

$$\frac{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}(i+j)p_4(i,j)}{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}p_4(i,j)} = \frac{\sum_{i=0}^{\infty}i(p_{ATBN}p_{828})^i \sum_{j=0}^{\infty}(p_{ATBN}p_{828})^j + \sum_{i=0}^{\infty}(p_{ATBN}p_{828})^i \sum_{j=0}^{\infty}j(p_{ATBN}p_{828})^j}{\sum_{i=0}^{\infty}(p_{ATBN}p_{828})^i \sum_{j=0}^{\infty}(p_{ATBN}p_{828})^j}$$

$$= \frac{2p_a p_8}{1-p_a p_8}.$$

For the typical values stated previously, the average value of $i + j$ for this linkage chains is ≈ 0.03. Structure 7 describes all possible pendant chains. Therefore, for the pendants, the average number of ATBN/828 pairs is

$$\frac{\sum_{i=0}^{\infty} i\, p_4(i)}{\sum_{i=0}^{\infty} p_4(i)} = \frac{\sum_{i=0}^{\infty} i\,(p_a p_8)^i}{\sum_{i=0}^{\infty} (p_a p_8)^i} = \frac{p_a p_8}{1 - p_a p_8}.$$

For the typical values stated previously, the average value of i in the pendant chains is ≈ 0.015.

Structure 8 describes all possible linear molecules. Therefore, for the linear molecules, the average number of ATBN/828 pairs is

$$\frac{\sum_{i=0}^{\infty} i\, p_5(i)}{\sum_{i=0}^{\infty} p_5(i)} = \frac{\sum_{i=0}^{\infty} i\,(p_a p_8)^i}{\sum_{i=0}^{\infty} (p_a p_8)^i} = \frac{p_a p_8}{1 - p_a p_8}.$$

For the typical values stated above, the average value of i is ≈ 0.015, and the average number of ATBN units in the linear molecules is ≈ 1.015. Therefore, most of the linear molecules contain just one ATBN unit and two monofunctional units (PGE or DFM).

3.5 Branched Molecules

Now that the length and rubber content of linkage and pendant chains are known, the molecular weight distribution of the branched copolymer can be predicted. The size distribution below the gel point for self condensing f functional units has been derived by Flory [6]. The fact that the PACM molecules in the resins of interest here are connected by linear structures will not affect the distribution of the number of PACM units linked together.

The number fraction of all copolymers molecules that contain x PACM units is

$$n_x = \frac{4 \alpha_B^{x-1}(1 - \alpha)^{2x+2}}{1 - 2\alpha_B} \frac{(3x)!}{(2x + 2)!\ x!}.$$

Using this expression, it can be found [3] that the number and weight average number of PACM units per molecule is

$$\overline{X}_n = \frac{1}{1 - 2\alpha}$$

and

$$\overline{X}_w = \frac{1 + \alpha}{1 - 3\alpha}.$$

$$\overline{X}_w = \frac{1+\alpha}{1-3\alpha} .$$

It should be noted that these results are limited to $\alpha_B < 1/3$ (pre-gelation). These results indicate that the weight average molecular weight (and the viscosity) will approach infinity when α_B approaches 1/3. It can easily be determined that each $x$mer must contain $2x + 2$ pendant chains and $x - 1$ linkage chains. When $\alpha_B = 0.3$, the weight average number of PACM units per molecule is 13. A molecule this size will contain 28 pendant chains and 12 linkage chains and have a molecular weight of about 19,000 g/mol.

3.6 Implications

It is predicted that for typical resin formulations, approximately 1.5% of pendant and linkage chains in the copolymer will contain ATBN rubber units. Approximately half of the ATBN units will be incorporated into the copolymer, while the other half will exist as a part of linear chains, most of which (>98%) will contain just one ATBN unit and two end caps (DFM or PGE). These rubber units will have a much higher mobility than the ATBN units that are incorporated into the copolymer chains, which on average contain 18 PACM units, 28 pendants, and 17 links.

4. Phase Equilibria

Butyl nitrile rubber is added to these resins to increase their toughness. It is well known that the presence of small, dispersed, rubber domains can greatly improve the toughness of brittle polymers. However, when all of the components are initially mixed, they are completely miscible with each other. The rubber will begin to phase separate into dispersed particles only after the epoxy/amine reaction has occurred to some extent. As this reaction progresses, the molecular weight of the epoxy copolymer increases [7, 8]. This increase in molecular weight decreases the entropy of mixing and favors phase separation of the rubber.

Phase separation in epoxy/rubber systems has been studied previously and predictions of the time evolution of particle formation have been made [7, 9]. However, the present resins will behave differently due to the presence of the difunctional monomer and the dimethacrylates. This section documents efforts to predict conditions under which the resins will phase separate.

4.1 Calculation of Solubility Parameters

In order to predict whether phase separation will occur, it is necessary to know the solubility parameters for the components. These were calculated for each

component before and after epoxy/amine reaction using a group contribution method using the procedures and data of van Krevelen [10].

The solubility parameter, δ, has units of $J^{1/2}/cm^{3/2}$. Table 1 provides the solubility parameters of the components before and after epoxy/amine reactions occur. Note that the solubility parameters of neither dimethacrylate (bisGMA and HDDMA) change because they do not react at this stage.

Table 1. Calculated solubility parameters of components before and after epoxy/amine reactions occur.

Component	δ ($J^{1/2}/cm^{3/2}$)	
	Before Reacting	After Reacting
Epon 828	18.15	20.62
PACM	18.69	18.01
ATBN	16.75	16.75
DFM	19.46	20.46
PGE	19.74	23.00
BisGMA	20.33	20.33
HDDMA	18.85	18.85

Binary interaction parameters, χ'_{ij}, between components i and j were calculated using

$$\chi'_{ij} = \frac{(\delta_i - \delta_j)^2}{RT},$$

where δ_i is the solubility parameter of component i, R is the gas constant, and T is the absolute temperature.

Since the phase behavior of these resins is most important at room temperature, χ' values before and after reaction are shown in Tables 2 and 3 at 20 °C. In general, larger positive values of χ' will favor phase separation.

Table 2. Binary interaction parameters, χ'(cm⁻³), between components before and after epoxy/amine reaction.

Component	Epon 828	PACM	ATBN	DFM	PGE	BisGMA	HDDMA
Epon 828		1.75 e⁻³	1.18 e⁻²	1.03 e⁻²	1.52 e⁻²	2.86 e⁻²	2.95 e⁻³
PACM	1.75 e⁻³		2.26 e⁻²	3.57 e⁻³	6.63 e⁻³	1.62 e⁻²	1.54 e⁻⁴
ATBN	1.18 e⁻²	2.26 e⁻²		4.42 e⁻²	5.38 e⁻²	7.71 e⁻²	2.65 e⁻²
DFM	1.03 e⁻²	3.57 e⁻³	4.42 e⁻²		4.71 e⁻⁴	4.55 e⁻³	2.24 e⁻³
PGE	1.52 e⁻²	6.63 e⁻³	5.38 e⁻²	4.71 e⁻⁴		2.09 e⁻³	4.76 e⁻³
BisGMA	2.86 e⁻²	1.62 e⁻²	7.71 e⁻²	4.55 e⁻³	2.09 e⁻³		1.32 e⁻²
HDDMA	2.95 e⁻³	1.54 e⁻⁴	2.65 e⁻²	2.24 e⁻³	4.76 e⁻³	1.32 e⁻²	

Table 3. Binary interaction parameters, χ' (cm^{-3}), between components after epoxy/amine reaction.

Component	Epon 828	PACM	ATBN	DFM	PGE	BisGMA	HDDMA
Epon 828		4.12 e^{-2}	9.02 e^{-2}	1.60 e^{-4}	3.40 e^{-2}	5.16 e^{-4}	1.89 e^{-2}
PACM	4.12 e^{-2}		9.47 e^{-3}	3.62 e^{-2}	1.50 e^{-1}	3.25 e^{-2}	4.29 e^{-3}
ATBN	9.02 e^{-2}	9.47 e^{-3}		8.28 e^{-2}	2.35 e^{-1}	7.71 e^{-2}	2.65 e^{-2}
DFM	1.60 e^{-4}	3.62 e^{-2}	8.28 e^{-2}		3.88 e^{-2}	1.02 e^{-4}	1.56 e^{-2}
PGE	3.40 e^{-2}	1.50 e^{-1}	2.35 e^{-1}	3.88 e^{-2}		4.29 e^{-2}	1.04 e^{-1}
BisGMA	5.16 e^{-4}	3.25 e^{-2}	7.71 e^{-2}	1.02 e^{-4}	4.29 e^{-2}		1.32 e^{-2}
HDDMA	1.89 e^{-2}	4.29 e^{-3}	2.65 e^{-2}	1.56 e^{-2}	1.04 e^{-1}	1.32 e^{-2}	

4.2 Free Energy of Mixing

The Flory-Huggins theory [11] will be used to predict the phase equilibria of these resins. The free energy change per unit volume of the solution, ΔG_m^v, associated with mixing N components to form a single phase is given by

$$\Delta G_m^v = \Delta H_m^v - T\Delta S_m^v,$$

where ΔH_m^v is the enthalpy of mixing per unit volume of the solution and ΔS_m^v is the entropy of mixing per unit volume of the solution. According to the Flory-Huggins theory, these are given by

$$\Delta H_m^v = RT\sum_{i=1}^{N}\sum_{j=i+1}^{N} \chi_{ij}'\phi_i\phi_j$$

and

$$\Delta S_m^v = RT\sum_{i=1}^{N}\frac{\phi_i}{v_i}\ln\phi_i,$$

where R is the gas constant, T is absolute temperature, ϕ_i is the volume fraction of component i, v_i is the molar volume of component i, and χ_{ij}' is the binary interaction parameter defined previously. ΔS_m^v is always negative, and this favors mixing (hinders phase separation). ΔH_m^v is usually positive, and this favors phase separation. The free energy of mixing per unit volume of the solution is then

$$\Delta G_m^v = RT\left(\sum_{i=1}^{N}\frac{\phi_i}{v_i}\ln\phi_i + \sum_{i=1}^{N}\sum_{j=i+1}^{N} \chi_{ij}'\phi_i\phi_j\right).$$

This equation will give the free energy change upon mixing of N components into a single phase. For the current resins of interest, this will apply only for the

initial mixture of components before the amine and epoxy groups begin to react. After the epoxy and amine reactions have occurred, a different approach is needed. After the epoxy/amine reaction, the resin will consist of only three components. These are bisGMA, HDDMA, and a random copolymer consisting of Epon 828, PACM, PGE, DFM, and ATBN units. The ATBN units are much longer than the others and are long enough to allow them to phase separate from the others. Therefore, the resins should be treated as though they are composed of four components—bisGMA, HDDMA, ATBN, and a random copolymer consisting of Epon 828, PACM, PGE, and DFM units.

Binary interaction parameters must now be determined between these four components to predict the phase separation behavior of the B-stage resins. When one or more of the components in a mixture are copolymers, the interaction parameter is usually designated B. The binary interaction parameters between the three pure components (bisGMA, HDDMA, ATBN) are just equal to the χ' values after reaction for those pairs.

In general, the binary interaction parameter between two copolymers I and J is calculated as follows. Assume that I is comprised of n_I different units and J is made up of n_J different units. Number the different units in I from 1 to n_I, and number the different units in J from n_I+1 through n_I+n_j. The interaction parameter B_{ij} between I and J is

$$B_{ij} = \sum_{k=1}^{n_I} \sum_{l=n_I+1}^{n_I+n_J} \chi'_{kl}\phi_k^I\phi_l^J - \sum_{k=1}^{n_I} \sum_{l=k+1}^{n_I} \chi'_{kl}\phi_k^I\phi_l^I - \sum_{k=n_J+1}^{n_I+n_J} \sum_{l=k+1}^{n_I+n_J} \chi'_{kl}\phi_k^J\phi_l^J,$$

where χ'_{ij} are the pure component binary interaction parameters and ϕ_k^I is the volume fraction of unit k in component I. If $n_I = n_J = 1$ (i.e., both components are pure), then B_{ij} just equals χ'_{ij} as stated above.

There is only one copolymer in the B-stage resin, so the case where $n_I > 1$ and $n_J = 1$ is of interest. For this case, the ϕ_k^J terms are zero because J is a pure component and

$$B_{ij} = \sum_{k=1}^{n_I} \chi'_{kj}\phi_k^I - \sum_{k=1}^{n_I} \sum_{l=k+1}^{n_I} \chi'_{kl}\phi_k^I\phi_l^I,$$

where i is the copolymer and j is one of the other components. This equation can now be used to calculate the interaction parameters between the copolymer and each of the other three components (bisGMA, HDDMA, and ATBN). These parameters are functions of the composition of the copolymer and will depend on the exact formulation of the resin. Values of the B parameters at 20 °C for a typical formulation ($R = 1$, $\alpha = 0.3$) are shown in Table 4.

Table 4. Binary interaction parameters, B (cm^{-3}), between components after epoxy/amine reaction for a typical formulation (R = 1, α = 0.3) at 20 °C.

Component	Copolymer	ATBN	BisGMA	HDDMA
Copolymer		5.82 e^{-3}	1.42 e^{-5}	1.10 e^{-3}
ATBN	5.82 e^{-3}		7.71 e^{-2}	2.65 e^{-2}
BisGMA	1.42 e^{-5}	7.71 e^{-2}		1.32 e^{-2}
HDDMA	1.10 e^{-3}	2.65 e^{-2}	1.32 e^{-2}	

The free energy of mixing of the B-stage resin can now be written as

$$\Delta G_m^v = RT\left(\sum_{i=1}^{N} \frac{\phi_i}{v_i} \ln \phi_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} B_{ij}\phi_i\phi_j \right),$$

with N (the total number of components) equal to 4. This expression can be used to generate a phase diagram that can be used to predict the conditions (compositions and temperatures), which will lead to phase separation.

The molecular weight of the copolymer affects ΔG_m^v through its molar volume that is proportional to molecular weight. As the molecular weight (and molar volume) of the copolymer increases as the epoxy/amine reactions occur, the $\frac{\phi_i}{v_i} \ln \phi$ term for the copolymer decreases and may cause phase separation to occur. However, the presence of the dimethacrylates (which do not react at this stage) will not allow the entropy of mixing to approach zero because their molar volumes remain constant and relatively small. HDDMA has a smaller molar volume (259 cm^3/mol) than bisGMA (480 cm^3/mol). Therefore, resins with larger amounts of dimethacrylates and larger HDDMA/bisGMA ratios will be less likely to phase separate. This effect has been observed experimentally.

4.3 Experimental Results

Resins with two different values of δ (0.4 and 0.63) but identical values of α (0.33), β (0.37), and γ (0.2) were each prepared with 10% and 15% ATBN rubber. These were mixed at room temperature for 10 min, cured at 60 °C for 12 hr, and degassed at 60 °C in a vacuum oven. Recall that δ is the ratio of the weight of bisGMA to the combined weight of bisGMA and HDDMA. In each case, the resins with δ = 0.63 were cloudy (almost opaque) in appearance after the epoxy/amine reaction was complete. The cloudy appearance is most likely due to light scattering by phase separated rubber particles and is a strong indication that phase separation has occurred. Both resins with δ = 0.4, however, were not cloudy and appeared transparent. Although transparency is not a definitive indication that phase separation did not occur, it indicates the possibility that it did not occur. Several resins were prepared without ARL1015 or PGE. These contained PACM, Epon 828, bisGMA, HDDMA, and between 5% and 15% ATBN

rubber. Of these resins, all of those with $\beta < 0.45$ appeared cloudy, while those with $\beta > 0.45$ were transparent. Recall that β is the ratio of epoxide units to dimethacrylate units. These observations support the prediction that increases in dimethacrylate content and in the HDDMA/bisGMA ratio decrease the tendency of these resins to phase separate.

Another interesting observation was noticed for the resins mentioned previously with $\delta = 0.4$. After curing and cooling to room temperature, these resins were transparent. However, when heated to 70 °C they became cloudy. When subsequently cooled, the cloudiness disappeared (*i.e.*, the change was reversible). This observation is an indication that these resins may have a lower critical solution temperature, and phase separation may occur as the resins are heated. This phase behavior cannot be predicted by the Flory-Huggins theory. It should be studied further because it could be used to induce formation of rubber particles before the resin is finally cured by exposure to an electron beam.

5. Effect of Radiation Exposure on Rubber Properties

The impact of electron beam exposure on the properties of nitrile rubber was investigated using dynamic mechanical analysis (DMA). Experiments were carried out using a TA Instruments DMA 2980. Samples approximately 20 mm long were loaded in the single cantilever configuration with an amplitude of 20 μm at a frequency of 0.1 Hz. Storage and loss moduli were recorded from -120° to 20 °C with a heating rate of 1 °C/min.

Simple formulations consisting only of Epon 828, PACM, and ATBN were used. These were mixed in stoichiometric ratios (two epoxides for each amine) and rubber fraction varied from 0% to 15%. These resins were cured at 60 °C for 12 hr. DMA was performed on these resins before and after exposure to an electron beam. The exposure was identical to the exposure used in the final curing of the one-part resins. The loss factor (tan δ) data for these resins are shown in Figures 2–5. The data for the unexposed resins is shown in Figure 3. The 0% rubber sample exhibits a maximum in tan δ at -57.3.

This peak can be attributed to the epoxy β relaxation [7]. The data for 10% and 15% rubber show shoulders near this temperature, and these can also be attributed to the epoxy β relaxation. These also show maxima at higher temperatures (-37.2 °C for 10% and -36.1 °C for 15%), which indicate the position of the glass transition temperature (T_g) of the nitrile rubber. Figures 3 and 4 show tan δ vs. temperature for the 10% and 15% rubber resins before and after exposure to the electron beam. After exposure, T_g of the rubber drops by
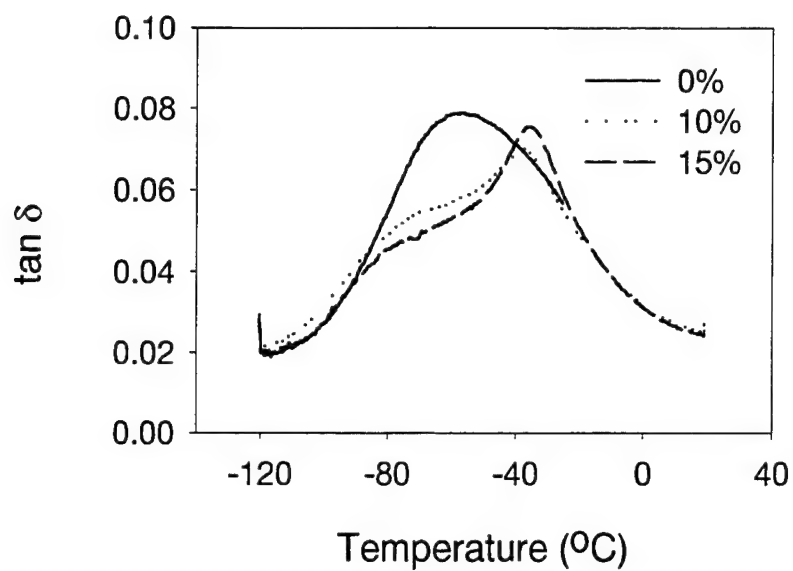
Figure 3. Tan δ as a function of temperature for cured epoxy resins containing differing amounts of nitrile rubber before exposure to e-beam.
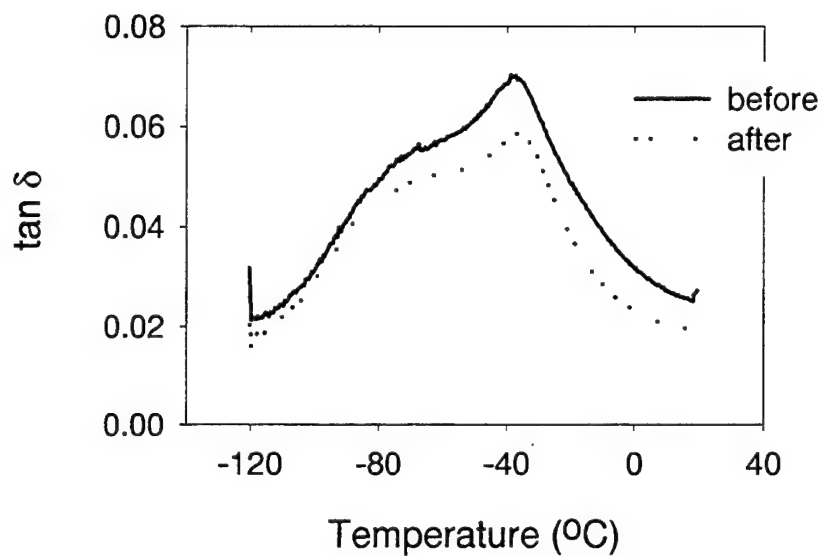

Figure 4. Tan δ as a function of temperature for cured epoxy resins containing 10% nitrile rubber before and after exposure to e-beam.
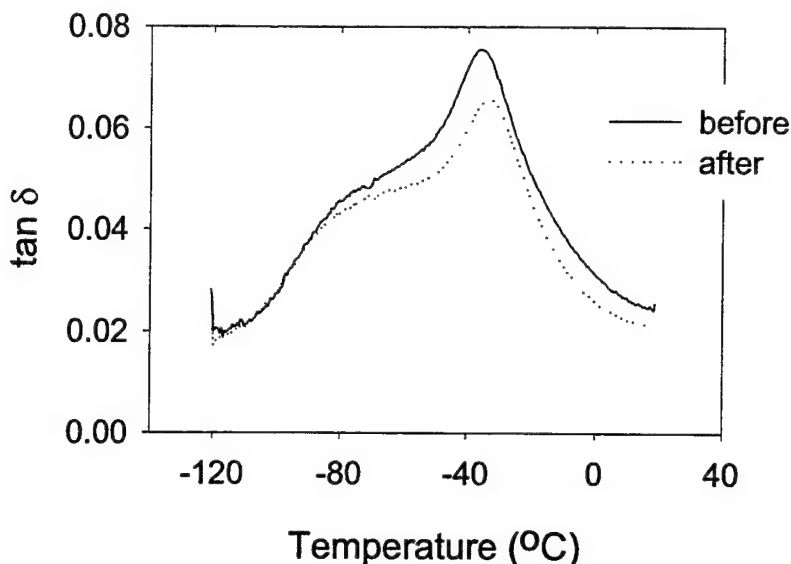
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Figure 5. Tan δ as a function of temperature for cured epoxy resins containing 15% nitrile rubber before and after exposure to e-beam.

1 °C in the 10% resin and 2.4 °C in the 15% resin. It was feared that exposure to the electron beam might cause the rubber to crosslink to a greater extent. This would adversely affect the ability of the rubber to toughen these resins. However, the small increases in T_g of the rubber after exposure indicates that little crosslinking is occurring, and the ability of the rubber to toughen these resins should not be affected.

6. Summary of Results, Conclusions, and Recommendations

Several issues related to the development of a radiation-curable rubber-toughened epoxy resin have been addressed. These issues are related to the properties of the B-stage resin (*i.e.*, after epoxy/amine reaction but before final curing by exposure to an electron beam.) The components of these resins were described, and a procedure was developed to determine the exact weight fractions of each component that must be mixed together to achieve desired branching coefficient and composition. Compositional variables include weight ratio of the two dimethacrylates, weight ratio of the two monoepoxides, and weight ratio of epoxides to dimethacrylates. Due to the nature of the production of one of the monoepoxides (the dual functional monomer), some formulations are not possible. More specifically, it is not possible to prepare these resins without either PGE or bisGMA. Using the developed procedure, a map of possible formulations was generated. This map shows the combinations of PGE and bisGMA content that are allowed and those that are not. A resin with a

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larger amount of PGE may have less bisGMA, while a resin with a lower amount of PGE must have more bisGMA. The addition of PGE will degrade the properties of the fully cured resin, while a minimum amount of bisGMA will limit the extent to which the viscosity of the B-stage resin can be controlled. Therefore, a compromise between reduced control of B-stage viscosity and final properties must be made. Procedures can be developed for similar resins with only slight modifications to the existing procedure.

A statistical analysis of the branched copolymer was performed to provide predictions for branching coefficient, copolymer molecular weight, and rubber connectivity for the B-stage resin. The copolymer consists of PACM units, which are each connected to four linear structures. These linear structures can be links between two PACM units or pendant chains, which are only connected to one PACM unit. It was predicted that for typical resin formulations, approximately 1.5% of pendant and linkage chains in the copolymer would contain ATBN rubber units. It was also predicted that approximately half of the ATBN units would be incorporated into the copolymer, while the other half would exist as parts of linear chains, most of which (>98%) contain just one ATBN unit and two end caps (DFM or PGE). These rubber units will have a much higher mobility than the ATBN units that are incorporated into the copolymer chains, which on average contain 18 PACM units, 28 pendants, and 17 links. The presence of these linear ATBN-containing molecules may cause the rate at which rubber particles coalesce to be unacceptably large. If the latter proves true, the use of an epoxide functional rubber would force all of the rubber to be connected to PACM units and hence to the branched copolymer. The coalescence rate of the rubber particles should be studied for these resins as functions of the branching coefficient and the HDDMA/bisGMA ratio. A decrease in the HDDMA/bisGMA ratio would result in an increase in the viscosity of the B-stage resin since bisGMA is more viscous that HDDMA. This would also reduce the coalescence rate. Coalesce rates for these resins can be measured using time-resolved laser light scattering or microscopy [12, 13].

The thermodynamics of phase separation of these resins was addressed. A procedure for determining the free energy of mixing, ΔG_m^v, of the initial mixture of components and the B-stage resin was described. This information can be used to generate a phase diagram for these resins that will predict the conditions (branching coefficient, temperature, resin composition) under which phase separation will occur. This is important because the mechanical properties of the fully cured resin will depend on the extent to which the ATBN rubber phase separates from the other components. Experimental results and preliminary predictions indicate that decreases in either the total dimethacrylate content or the HDDMA/bisGMA ratio lead to an increased tendency towards phase separation of the rubber. It is recommended that modeling and experimental determination of the phase behavior of these resin be studied further.

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Generation of the phase diagram will allow the compositions of the matrix and particulate phases to be predicted as functions of dimethacrylate content, branching coefficient, and temperature. Some of these resins appeared to exhibit a lower critical solution temperature. That is, phase separation appeared to occur when the temperature was raised approximately 50 °C above ambient and disappear when cooled back to ambient temperature. B-stage resins that exhibit this type of behavior may have practical applications. Since they exist as a single phase at ambient temperature, the problem of coalescence is avoided while being stored at ambient temperature. The resins could then be heated immediately before the final curing step to achieve the desired phase separation.

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13. ABSTRACT (Maximum 200 words)

Several issues related to the development of a radiation-curable rubber-toughened epoxy resin are investigated by performing a statistical analysis of semi-interpenetrating polymer blend formulations. The statistical analysis provided predictions for branching coefficient, copolymer molecular weight, and rubber-to-network connectivity for the B-staged interpenetrating networks. These statistical metrics relate to the properties of thermally generated B-stage networks, prior to secondary network formation using radiation cure methods, such as electron beam or ultraviolet excitation. The components of these resins were described, and a procedure was developed to determine the exact weight fractions of each component that must be mixed together to achieve a desired branching coefficient and resin composition. Compositional variables include weight ratio of the two dimethacrylates, weight ratio of the two monoepoxides, and weight ratio of epoxides to dimethacrylates. Using the raw materials selected for this study, we determined that many network structures are not attainable. Specifically, it is not possible to prepare B-stage resins without the use of mono- or difunctional units, such as phenyl glycidyl ether (PGE) or methacrylated digicydyl ether of bisphenol A (bisGMA). The possible formulations are determined, and a map is proposed showing the combinations of PGE and bisGMA content that are allowed for B-stage formation.

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